Thermophysical properties of a $Cu_{46}Zr_{42}Al_7Y_5$ bulk metallic glass-forming liquid

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(Received 29 March 2006; accepted 4 May 2006; published online 31 May 2006)

The thermophysical properties, including the specific volume V, the surface tension σ, and the viscosity η, of a $Cu_{46}Zr_{42}Al_7Y_5$ bulk metallic glass in the molten state were investigated using a containerless high-temperature high-vacuum electrostatic levitation technique. The viscosity measurements indicate that the $Cu_{46}Zr_{42}Al_7Y_5$ alloy exhibits an intermediate fragility with the fragility index $m=49$. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2208550]

Bulk-metallic glasses (BMGs) often show an extraordinarily high strength and low room-temperature ductility.[1–3] Recent studies indicated that the room-temperature ductility of BMG alloys is intrinsically related to their low Poisson's ratio.[4–6] Pd-, Pt-, and Au-based BMG alloys show a good ductility compared with other BMG alloys due to a high Poisson's ratio of these alloys (≈ 0.4).[4,7] Nivikov and Sokolov[8] reported that Poisson's ratio of glasses at room temperature is closely related to the fragility of glass-forming liquids, which measures the steepness of viscosity changes with the temperature. Compared with a strong liquid, a fragile liquid shows a steeper change in the viscosity around the glass-transition temperature T_g, and a smoother change in the viscosity around the melting temperature T_m.[9] Taken together, the viscosity change at high temperatures may be associated with the room-temperature mechanical properties. A fragile liquid with a high value of Poisson's ratio is expected to exhibit good room-temperature ductility. Moreover, according to the classical nucleation theory,[10] the viscosity at high temperatures, along with other thermophysical properties, will influence the glass-forming ability (GFA) of liquids. Therefore, the thermophysical properties (i.e., the specific volume V, the surface tension σ, and the viscosity, η) of the glass-forming liquids are important parameters, which help understand both the room-temperature mechanical properties and the GFA.

In this letter, we reported the measurements of the thermophysical properties of a $Cu_{46}Zr_{42}Al_7Y_5$ bulk metallic glass-forming liquid using a containerless high-temperature high-vacuum electrostatic levitation (ESL) technique. The $Cu_{46}Zr_{42}Al_7Y_5$ BMG alloy shows a good GFA with a maximum thickness of 10 mm when fabricated using the copper-mold casting.[11]

The master $Cu_{46}Zr_{42}Al_7Y_5$ alloy was prepared by melting a mixture of the high-purity Cu (99.999%), Zr (99.9%), Ti (99.99%), Al (99.999%), and Y (99.99%) in a mini arc-melter under a Ti-gettered argon gas atmosphere. To ensure the homogeneity, the samples were melted for at least five times. Calorimetric measurements indicate $T_g=675$ K and $T_m=1123$ K for the as-cast $Cu_{46}Zr_{42}Al_7Y_5$ BMG alloy. A sample of about 20 mg was levitated between a pair of electrodes in the ESL, which was evacuated to 10^{-8} torr. The BMG sample was heated by a high-power cw Nd: YAG (yttrium aluminum garnet) laser, and was cooled by turning off the laser power completely. The temperature of the sample was determined using a two-color pyrometer. The specific volumes of the liquid and crystal were measured by monitoring the sample volume evolution using a change-coupled device (CCD) camera with a telescopic head. The surface tension and the viscosity of the molten drop were measured by inducing the resonant oscillation using an ac electric field. The detailed experimental procedures of the ESL experiments were described elsewhere.[12–14]

Figure 1(a) shows the cooling and heating curves of the $Cu_{46}Zr_{42}Al_7Y_5$ molten drop as well as the specific volume changes with the time. The sample was initially heated to the liquid state at 1520 K and subsequently cooled to 1049 K with an undercooling for about 74 K. After the recalescence due to the crystallization, the crystalline solid was continuously cooled to 804 K. The crystallization also causes an abrupt drop in the specific volume. Second heating-cooling cycle from 40 to 95 s shows similar results. The corresponding specific volume of the liquid and the crystal as a function of temperature is shown in Fig. 1(b). The specific volume of the liquid and the crystal shows a linear relationship with the temperature, which can be described by an equation with the form,[13]

$$V(T) = V_m[1 + \alpha(T - T_m)], \tag{1}$$

with α the thermal-expansion coefficient and V_m the specific volume at the melting temperature T_m. The best fit yields $V_m{}^L=0.1512$ cm^3 g^{-1} and $\alpha^L=6.36\times10^{-5}$ K^{-1} for the liquid, and $V_m{}^C=0.1488$ cm^3 g^{-1} and $\alpha^C=3.54\times10^{-5}$ K^{-1} for the crystal. The specific volume difference $\Delta V_m{}^{L-C}$ at the T_m is $V_m{}^L-V_m{}^C=0.0024$ cm^3 g^{-1}, which is much smaller than the

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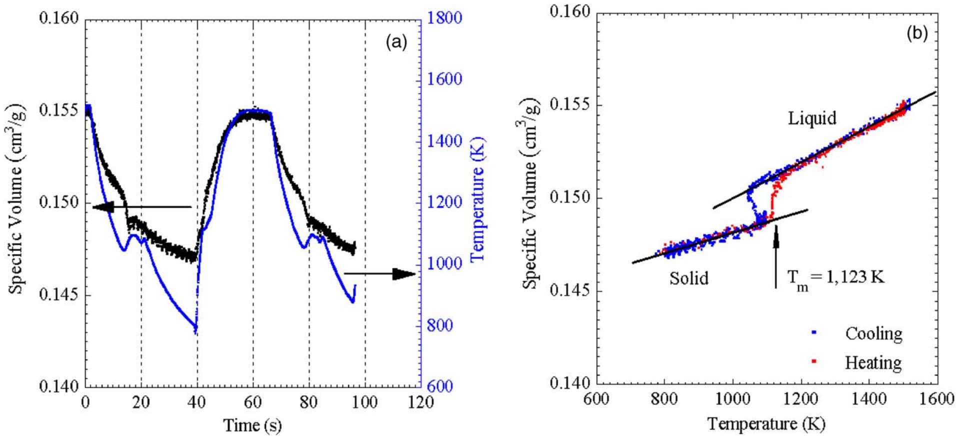

FIG. 1. (Color online) Cooling and heating curves and the specific volume of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy (a) and the specific volume of the liquid and crystal as a function of temperature (b). The solid lines in (b) are linear fits using Eq. (1).

binary alloy systems and is comparable with other multicomponent BMG alloys, such as Vit 105 and Vit 106.[14] These results indicate that multicomponent $Cu_{46}Zr_{42}Al_7Y_5$ alloy has a relatively dense liquid structure, which favors the glass formation.

The surface tension and the viscosity of the liquid drop, measured as a function of temperature using a drop oscillation technique in the ESL, are presented in Fig. 2. The surface tension [Fig. 2(a)] exhibits a linear relationship with the temperature, which can be described by $\sigma=1.119-(2.924\times10^{-5})T$ (N m^{-1}). Previous studies indicated that some multicomponent glass-forming liquids show a positive temperature dependence, which was attributed to the alloy-element segregation leading to a low surface tension at a low temperature.[14] The present study indicates that the surface tension of the $Cu_{46}Zr_{42}Al_7Y_5$ liquid has a negative temperature dependence.

The viscosity over the wide temperature range from T_g to above T_m was frequently fitted using a Vogel-Tammann-Fulcher (VTF) equation with the form[15–17]

$$\eta=\eta_0\exp\left(\frac{DT}{T-T_0}\right), \tag{2}$$

where η_0 and T_0 are constants and D is a fragility index. A fragile liquid has a D value in the range of 1–10, while it ranges from 20 to 100 for a strong liquid.[9] T_0 is often smaller than T_g, and approximately equals to the Kauzmann temperature T_K, at which the excess entropy for the liquid diminishes with respect to the crystal.[18] The viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy at T_g is 10^{12} Pa s, while the viscosity in the vicinity of T_g is not available. The application of the VTF equation to the viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy from the glass transition to the molten liquid yields $\eta_0=5.6\times10^{-3}$ Pa s, $D=2.7$, and $T_0=623$ K. Apparently, the VTF equation is not suitable to describe the viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy, since the very low D value would imply that $Cu_{46}Zr_{42}Al_7Y_5$ alloy is extremely fragile, which is not the case, based on its measured value of the viscosity from the molten liquid ($\sim$0.1 Pa s). The viscosity of the liquid around T_m is closely related to the fragility of glass-forming liquids. A fragile liquid has a lower value of the viscosity around T_m. The most fragile liquid, such as 0-terphenyl (OTP), has a viscosity of about 0.01 Pa s at T_m, which is about one order of magnitude smaller than the $Cu_{46}Zr_{42}Al_7Y_5$ alloy.

More recently, a cluster model describing the viscous flow of glass-forming liquids was proposed.[19] It is assumed that a supercooled liquid contains some solidlike clusters. The glass transition is due to the large scale of the cluster formation throughout the supercooled liquid. Within the cluster model, the viscosity above T_m obeys an Arrhenius law with the form

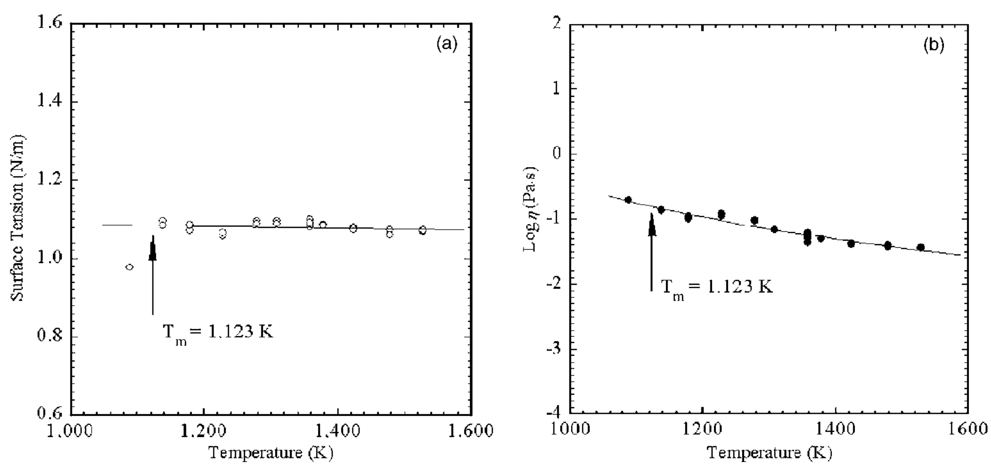

FIG. 2. The surface tension (a) and the viscosity (b) of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy as a function of temperature. The solid line in (a) was fitted by $\sigma=1.119-(2.924\times10^{-5})T$. The solid line in (b) is fitted using Eq. (3).

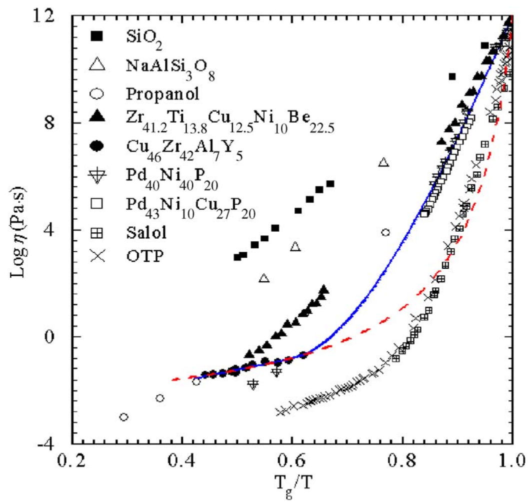

FIG. 3. (Color online) The Angell plot (Ref. 20) of the viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy and other glass-forming liquids ranging from the strong extreme such as SiO_2 and fragile extreme such as OTP. The viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy was compared with some BMG alloys including Vit 1 (Ref. 22) and Pd-based alloys (Refs. 26, 30, and 31). The viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy was fitted using Eq. (2) (red dashed line) and using Eqs. (3) and (4) (blue solid line). While both fits agree well with the measured data at the high temperature range, Eq. (2) did not provide reasonable extrapolation of the viscosity at the lower temperature range, yielding very low viscosity and D values.

$$\eta(T) = \eta_1 \exp\left(\frac{E_1}{k_B T}\right), \tag{3}$$

where η_1 is a constant, E_1 is the activation energy for the viscous flow of the liquid above T_m, and k_B is the Boltzmann constant. The best fit of the data shown in Fig. 2(b) yields $\eta_1 = 4.54 \times 10^{-4}$ Pa s and $E_1 = 0.57$ eV. With decreasing temperature from T_m to T_g, the viscosity starts to deviate from the Arrhenius relation due to the solidlike cluster formation. A fitting equation for the viscosity below T_m was derived with a form

$$\eta = \eta_2 \exp(E_2/k_B T)\exp(\Phi T/T_g), \tag{4}$$

where η_2 is a constant, E_2 is the activation energy, and Φ is another fragility parameter. Equation (4) indicates that the viscosity below T_m contains an Arrhenius term and a fragility term. A more fragile liquid has a larger value of Φ. The best fit of the viscosity below T_m yields $\eta_2 = 6.17 \times 10^{-88}$ Pa s, $E_2 = 9.92$ eV, and $\Phi = 57.94$.

The fragility of the glass-forming liquids has been extensively investigated in various liquids[9,20,21] including the bulk metallic glass-forming liquids,[1,18,22–28] which is closely related to Poisson's ratio and the liquid dynamics. There are different ways to quantify the fragility of glass-forming liquids, i.e., fragility parameters in Eqs. (2) and (4). For the convenience of the direct comparison with other glass-forming liquids, a fragility index m, introduced by Böhmer *et al.*[29] will be employed. m was defined as

$$m = \left.\frac{d \log \eta}{d(T_g/T)}\right|_{T=T_g}. \tag{5}$$

More fragile liquids have a larger value of m (60–150). The m value can be obtained from the T_g-scaled Angell plot in Fig. 3.[20] The strong extreme, such as SiO_2, and the fragile extreme, such as OTP, are included in Fig. 3. For comparison, the typical BMG alloys including Zr-based Vit 1 (Ref. 22) alloy and Pd-based alloys[26,30,31] are also included. The m value is calculated to be 49 for the $Cu_{46}Zr_{42}Al_7Y_5$ alloy, indicating that this alloy exhibits an intermediate fragility. As shown in Fig. 3, the viscosity values of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy at high temperature are lower than those of very viscous liquids such as Zr-based Vit 1 alloy,[22] and are higher than those of relatively fragile liquids such as Pd-based BMG alloys.[26,30,31]

In summary, the thermophysical properties of the molten $Cu_{46}Zr_{42}Al_7Y_5$ liquid have been measured using a containerless high-temperature high-vacuum ESL technique. The viscosity of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy cannot be adequately fitted by the VFT equation, and can be described by the recently proposed cluster model. The fragility index m of this alloy is determined to be 49.

This work was supported by the National Science Foundation (NSF) International Materials Institutes (IMI) Program (DMR-0231320).

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